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## Emission patterns and spatiotemporal variations of halocarbons in the Pearl River Delta region, southern China

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[1] On 8 selected days between 25 October and 1 December 2007, 198 whole air samples were simultaneously collected at two sites in the greater Pearl River Delta (PRD), namely, Wan Qing Sha (WQS) in inland PRD and Tung Chung (TC) in Hong Kong, for the evaluation of halocarbons including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and other chlorinated compounds. The mean mixing ratios of CFC-12, CH<sub>3</sub>CCl<sub>3</sub>, CH<sub>3</sub>Br, C<sub>2</sub>HCl<sub>3</sub>, and C<sub>2</sub>Cl<sub>4</sub> at WQS were much higher than those at TC ( $p < 0.001$ ), while HCFC-22 was higher at TC ( $p < 0.01$ ). Long-lived species such as CFC-11, CFC-12, and CFC-113 showed similar temporal patterns on most sampling days with small daily variation, whereas the main species used as solvents such as C<sub>2</sub>HCl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub> presented large daily variations though with consistent temporal patterns. Source profile analysis revealed that although there was no remarkable change in emission sources between 2001–2002 and 2007, the emissions of CFCs and CCl<sub>4</sub> from the production of refrigeration in 2007 were 1.4–2.0 times those in 2001–2002, and the use of HCFC-22 has significantly increased in these years while the use of C<sub>2</sub>HCl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub> in the electronics industry showed a remarkable reduction. By comparing the halocarbon data collected in this study with those observed by other research teams in recent years, we found that the levels of CFCs have declined since 2001, while their substitute HCFC-22 has increased in emissions in recent years, especially in Hong Kong. The annual trends are consistent with the implementation of the Montreal Protocol. The results obtained in this study provide useful information to local government on effective control of halocarbon emissions in this region.

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### 1. Introduction

[2] In the early 1970s, Molina and Rowland [1974] first theorized that chlorine compounds, manufactured as refrigerants and aerosol propellants, could destroy the stratospheric ozone layer. This hypothesis was confirmed in 1985 by a measurement of large seasonal depletion of stratospheric ozone over Antarctica [Farman et al., 1985; Solomon et al., 1986]. Some observations have shown that the atmospheric loading of ozone depleting halocarbons in the lower atmosphere is currently in decline because of large reductions in the global production and emissions of ozone-depletion substances (ODSs) by developed countries during the 1990s

[Elkins et al., 1993; Montzka et al., 1996, 1999, 2003; Cunnold et al., 1997; UNEP, 2002; Yokouchi et al., 2002a; World Meteorological Organization, 2003; Hurst et al., 2004]. This indicates effective control of ODSs due to the Montreal Protocol and its amendments and adjustments [Solomon, 1999; Weatherhead and Andersen, 2006; Eyring et al., 2007]. In recent years, controls on ODSs have often focused on returning effective equivalent stratospheric chlorine (EESC) to the level that prevailed in 1980 [Weatherhead and Andersen, 2006]. EESC is a convenient parameter to quantify the effects of halogens (chlorine and bromine) on ozone depletion in the stratosphere [Newman et al., 2007]. The turnaround in EESC suggests that the early signs of an ozone layer recovery may be detected in the early 21st century [Weatherhead et al., 2000; Reinsel et al., 2002]. Due to the different features and different use patterns for different halocarbon species, the road to ozone recovery remains uncertain [Fraser and Prather, 1999; Montzka et al., 1999].

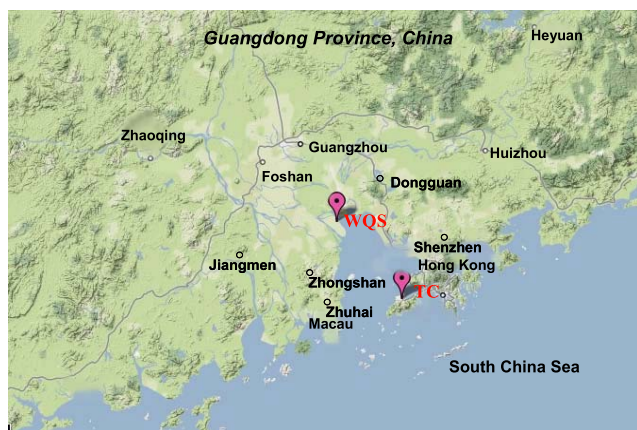
[3] Chlorofluorocarbons (CFCs) and other halocarbons have been used as refrigerants, propellants and solvents since the early and middle twentieth century. Although the Montreal Protocol imposed a total ban on production and consumption of these species in developed countries in 1996

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**Figure 1.** Location of the sampling sites in the Pearl River Delta of southern China.

[United Nations Environment Programme (UNEP), 1998], developing countries are subject to a step-by-step reduction in production and consumption [UNEP, 2002]. Both leakage from old refrigeration and air conditioning systems and direct emissions from production, associated with those species with long atmospheric lifetimes, have resulted in a steady accumulation of CFCs in the atmosphere [Fraser and Prather, 1999]. Among the CFC-replacement compounds, HCFC-22 (chlorodifluoromethane,  $\text{CHF}_2\text{Cl}$ ) is the most abundant hydrochlorofluorocarbon (HCFC) measured in the atmosphere, globally averaging 140–145 pptv in 2000 and growing at 5 pptv/yr [Montzka et al., 1999; Prinn et al., 2000; Sturrock et al., 2001; O'Doherty et al., 2004]. The principal use of HCFC-22 is as a commercial product in refrigeration and foam blowing applications, from which it is eventually released into the atmosphere. Emissions of carbon tetrachloride ( $\text{CCl}_4$ ) originate primarily from its use as a chemical feedstock for the production of CFC-11. The Montreal Protocol called for a total ban of this halocarbon in developed countries by 1996, while restrictions in developing countries were scheduled to start in 2005.  $\text{CH}_3\text{CCl}_3$  is a halocarbon of particular interest as it plays a role in stratospheric ozone depletion as well. Its trends are used to deduce average levels of hydroxyl radical (OH), the main atmospheric oxidant for many environmentally important gases [Prinn et al., 1995, 2001, 2005; Krol et al., 2003; Palmer et al., 2003; Bousquet et al., 2005; Wang et al., 2008]. Though it was banned under the Montreal Protocol due to its high ozone-depletion potential (ODP), there are some signs of continuous emissions of  $\text{CH}_3\text{CCl}_3$  in Europe [Gros et al., 2003; Krol et al., 2003; Reimann et al., 2005] and North America [Millet and Goldstein, 2004; Hurst et al., 2006; Millet et al., 2009]. Trichloroethene (TCE) and perchloroethylene (PCE) are used as industrial solvents and degreasers and are excellent markers of anthropogenically polluted air. Due to their short atmosphere lifetimes (0.01 and 0.27 years, respectively) [Warneck, 2000] and low impact on stratospheric ozone, they are not controlled by the Montreal Protocol, but they are hazardous and toxic organic compounds affecting human health (Agency for Toxic Substances and Diseases Registry, <http://www.atsdr.cdc.gov/toxfaqs/index.asp>). In addition, Dimmer et al. [2001] reported possible oceanic emissions of TCE in subtropical

oceans. Methyl chloride ( $\text{CH}_3\text{Cl}$ ) and methyl bromide ( $\text{CH}_3\text{Br}$ ) have both strong anthropogenic and natural sources.  $\text{CH}_3\text{Cl}$ , the most abundant halocarbon in the atmosphere, has received much attention as a natural source of chlorine atoms in the stratosphere [Fabian, 1986; Graedel and Keene, 1995]. Current estimates of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  emissions from oceanic sources, terrestrial plants and fungi, biomass burning and anthropogenic input do not balance their losses, which are due to oxidation by hydroxyl radicals, oceanic degradation, and consumption in soils, suggesting that additional natural terrestrial sources may be important [Moore, 2000; Yokouchi et al., 2000, 2002a; Andreae and Merlet, 2001; Hamilton et al., 2003]. Coastal salt marshes and tropical coastal land are also apparently important sources of methyl halides [Rhew et al., 2000, 2001, 2007; Yokouchi et al., 2000, 2002b; Bill et al., 2002; Rhew and Abel, 2007].

[4] China is one of the most populated, industrialized, and fastest developing countries, classified as a Montreal Protocol's "Article 5 Party." Namely, China is allowed to produce and consume ODSs. Under the Montreal Protocol, China has been required to phase out 50% of the 1995–1997 average level of CFCs production and consumption by 2005, and 100% (based on the same baseline) by 2010. In the past decade, international attention has been focused on halocarbon emissions in China, including the Pearl River Delta (PRD) region [e.g., Blake et al., 2003; Palmer et al., 2003; Barletta et al., 2006; Qin, 2007; Guo et al., 2009a; Stohl et al., 2009, 2010; Vollmer et al., 2009]. For instance, Stohl et al. [2009, 2010] reported that HCFC-22 emission for China in 2006 was 71 kt/yr and 65.3 kt/yr in 2008, whereas Vollmer et al. [2009] estimated the HCFC-22 emission in China in 2007 was 165 kt/yr. The PRD region is one of the most developed regions in China. It is also a leading manufacturing center in south China. The greater PRD region consists of nine cities within Guangdong Province (usually these nine cities are considered to comprise the inland PRD region), plus Hong Kong and Macau, as shown in Figure 1. The industries in the PRD manufacture a wide variety of goods, from electronics and air conditioners to refrigerators and automobiles. All these developments have led to deteriorated air quality in the region. High levels of ozone and its precursors, and low visibility on a regional scale have been reported [Wang and Kwok, 2003; Wang et al., 2005; Streets et al., 2006]. Significant enhancement of most halocarbons has been found in this region due to their increased production and extensive industrial uses [Chan and Chu, 2007]. Guo et al. [2009a] identified solvent use and refrigeration as major halocarbon sources in this region. As a "non-Article 5" party, Hong Kong was required to totally phase out ODSs by 1996 on the basis of the Montreal Protocol. Since the inland PRD region implements a different ODS phase out schedule than Hong Kong, and because these two regions are geographically close, it is important to inspect how the two regions are affected under different phase out schedules.

[5] A comprehensive field measurement campaign was carried out at two sites simultaneously in the greater PRD, namely Wan Qing Sha (WQS) in inland PRD and Tung Chung (TC) in Hong Kong, from 25 October to 1 December 2007. In total 198 whole air samples were collected. Using these data, the levels of individual trace gases, total non-methane hydrocarbons (NMHCs), and total carbonyls in

both areas were reviewed, and the differences and relationships of various air pollutant concentrations at the two sites were discussed [Guo *et al.*, 2009b]. Here, we mainly analyze the halocarbon data collected at these two sites during the sampling period. The emission patterns and spatiotemporal variations of halocarbons are discussed, and the regional transport influence on the halocarbons at both sites is assessed. Finally, the annual trends of major halocarbons in recent years are shown using data collected earlier in the study region by our team and other collaborative groups. To our best knowledge, this is the first time that annual trends of halocarbons have been obtained for this region.

## 2. Methodology

### 2.1. Description of the Sampling Sites

[6] The inland PRD region (42,000 km<sup>2</sup>) is situated within Guangdong province in southern China on the Tropic of Cancer (23.5°N), and is composed of nine cities. Two sampling sites, i.e., Wan Qing Sha (WQS) in inland PRD and Tung Chung (TC) in Hong Kong, were selected for field measurements for the purpose of better understanding the interplay of air masses between inland PRD and Hong Kong (Figure 1). The distance between the two sites is about 62 km. The WQS (22.711°N, 113.549°E) site, a small town in southernmost Guangzhou, is located at the centre of the PRD. This small town is surrounded by farmlands and has very few textile and clothing workshops, so the local anthropogenic emissions are not remarkable. The major pollutants are mainly from the surrounding cities. The site is 50 km southeast of the Guangzhou urban center, 40 km southwest of Dongguan, 50 km northwest of Shenzhen, and 25 km northeast of Zhongshan, making it a good location to characterize the air pollution in inland PRD. Large amounts of halocarbons are frequently used in these urban centers as cleaning solvents, refrigerants and industrial feedstock [e.g., Chan and Chu, 2007; Chang *et al.*, 2008]. The measurements were carried out on the rooftop of a 15 m building.

[7] TC (22.30°N, 113.93°E) is located on northern Lantau Island, about 3 km south of the Hong Kong International airport at Chek Lap Kok. It is a newly developed residential town but adjacent to the highway and to railway lines. It is about 20 km southwest of the Hong Kong urban center and 38 km northeast of Macau. In addition to local emission sources, TC is also affected by the polluted continental air masses from the highly industrialized PRD region of mainland China. Thus, this site is capable of monitoring air pollutants transported from the inland PRD region and is suitable for assessing their impact on local air quality. The samples were collected on the rooftop of a 15 m building. For more details, please refer to Guo *et al.* [2009b].

### 2.2. Sampling and Chemical Analysis

#### 2.2.1. Halocarbons

[8] Ambient halocarbon samples were collected using cleaned and evacuated 2-L electro-polished stainless steel canisters on selected days when O<sub>3</sub> mixing ratios were high (i.e., 26–27 October, 13 November, 15–17 November, 23 November, and 1 December), in keeping with the aim of this study to investigate poor air quality days. These potential high-O<sub>3</sub> episode days were selected on the basis of weather prediction and meteorological data analysis, which were

usually related to stronger solar radiation, weaker wind speed and less vertical dilution of air pollution, compared to non-O<sub>3</sub> episode days. Details of the preparation and preconditioning of the canisters are described in Blake *et al.* [1994]. During sampling, a flow controlling device was used to collect 1 h integrated samples. Hourly integrated air samples were collected from 0700 to 1400 LT at TC and from 0600 to 1400 LT at WQS on the selected days.

[9] The samples were analyzed by an Entech Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) coupled with a gas chromatography-mass selective detector (GC-MSD, Agilent 5973N). The preconcentration step was the same as described by Yi *et al.* [2007]. Briefly, the preconcentrator had multistage traps to remove H<sub>2</sub>O and CO<sub>2</sub>. The first trap was cooled to −160°C by liquid nitrogen. When air samples were firstly drawn through this trap, O<sub>2</sub> and N<sub>2</sub> passed through the trap, while all target compounds plus H<sub>2</sub>O and CO<sub>2</sub> were trapped. After trapping, this primary trap was heated to 10°C and at this temperature H<sub>2</sub>O should be in liquid state. The pure helium carried all the target compounds and CO<sub>2</sub>, through a process called micro-purge and trap, to the secondary trap at −40°C with Tenax as adsorbents. Most H<sub>2</sub>O stayed in the primary trap and CO<sub>2</sub> passed through the secondary trap, while all target compounds were trapped in the secondary step. After the micro-purge and trap, the secondary trap was heated to 180°C and all target compounds were desorbed and brought by helium to a tertiary trap at −170°C. This tertiary trap is necessary for better separation of compounds in GC and for better shapes of GC peaks. A HP-1 capillary column (60 m × 0.32 mm × 1.0 μm, Agilent Technology, USA) was used with helium as carrier gas. The GC oven temperature was initially programmed at −50 °C, holding for 3 min, increasing to 10 °C at 15 °C min<sup>−1</sup>, then to 120 °C at 5 °C min<sup>−1</sup>, and finally to 250°C at 10°C min<sup>−1</sup>, holding for 10 min. The MSD was operated in selected ion mode (SIM) with electron impact (EI) ionization. The identification of each compound was based on its retention time and mass spectrum. Target compounds were quantified by using multipoint external calibration method. To prepare calibration curves, a 100 ppbv Method TO-14A calibration gas standards (Spectra Gases, Inc., Branchburg, New Jersey, USA) was dynamically diluted with pure nitrogen to 0 (pure nitrogen), 100 pptv, 500 pptv, 2000 pptv and 4000 pptv using mass flow controllers. The diluted gas standards were analyzed in the same way as the field samples. The correlation coefficients of the target compounds in the calibration curves were 0.995–0.999. The halocarbon detection limit is 1 pptv, and all halocarbons in all the samples were present at mixing ratios well above their detection limits. The precision of the halocarbon measurements varied compound by compound and was 1% for CFCs and CCl<sub>4</sub>; 3% for HCFC-22; and 2% for CH<sub>3</sub>CCl<sub>3</sub>, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, C<sub>2</sub>HCl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub>. The measurement accuracy was determined by the difference between the measured and true values of the standard gases. The measurement accuracy also varied by compound and was 2% for CFCs; 10% for HCFC-22 and C<sub>2</sub>Cl<sub>4</sub>; and 5% for CH<sub>3</sub>CCl<sub>3</sub>, CCl<sub>4</sub>, CH<sub>3</sub>Cl and CH<sub>3</sub>Br.

#### 2.2.2. Trace Gases

[10] At TC, O<sub>3</sub>, CO, SO<sub>2</sub>, NO and meteorological parameters were measured at a monitoring station operated by the Hong Kong Environmental Protection Department

(HKEPD). This station uses similar instruments and quality assurance and control protocols to those in the US air quality monitoring program (<http://epic.epd.gov.hk/ca/uid/airdata>). At WQS, measurement instruments were installed in a room of the building, beneath the rooftop. Ambient air samples were drawn through a 5 m long perfluoroalkoxy (PFA) Teflon tube (OD: 12.7 mm; ID: 9.6 mm). The inlet of the sampling tube was located 2 m above the rooftop of the building. The other end of the sampling tube was connected to a PFA manifold with a bypass pump drawing air at a rate of 15 L min<sup>-1</sup>. The intake of the analyzers for O<sub>3</sub>, CO, SO<sub>2</sub> and NO was connected to the manifold. A detailed description of the in situ measurements of O<sub>3</sub>, CO, SO<sub>2</sub>, and NO is provided elsewhere [Wang *et al.*, 2002]. Briefly, O<sub>3</sub> was measured using a commercial UV photometric analyzer (Thermo Environmental Instruments (TEI), model 49C) with a detection limit of 2 ppbv. SO<sub>2</sub> was measured by a pulsed UV fluorescence (TEI, model 43S) with a detection limit of 0.06 ppbv. NO and NO<sub>x</sub> were detected using a chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer (Thermo Electron Corporation, Model 42i trace level) with a detection limit of 0.05 ppbv. For the O<sub>3</sub>, SO<sub>2</sub>, NO and NO<sub>x</sub> analyzers, a data logger (Environmental Systems Corporation, Model 8816) was used to control the calibrations and to collect data, which were averaged to 1 min values.

[11] In addition to the above chemical measurements, several meteorological parameters were monitored by an integrated sensor suite (Vantage Pro TM & Vantage Pro 2 Plus TM Weather Stations, Davis Instruments), including wind speed and direction, temperature, relative humidity and solar radiation.

### 2.2.3. Measurements of Boundary Layer Height

[12] The Hong Kong University of Science and Technology (HKUST) operates two lidar systems at Yuen Long and Sha Tau Kok, Hong Kong. The lidar system monitors the evolution of the atmospheric boundary layer using aerosols as the tracers of atmospheric motion. Hence, it can provide information on the boundary layer height. The real-time data of the lidar systems were downloaded from the HKUST website for the sampling period (<http://envf.ust.hk/dataview/others/current/>).

### 2.3. Quality Control and Assurance

[13] Before sampling, all canisters were cleaned at least five times by repeatedly filling and evacuating humidified zero air. In order to check if there was any contamination in the canister, we filled each evacuated canister with pure N<sub>2</sub> and stored them in the laboratory for at least 24 hours. These canisters were then checked by the same VOC analytical method to ensure that all target compounds were not found or were under the method detection limit. Duplicate samples were regularly collected to check the precision and reliability of the sampling and analytical methods. The relative standard deviation (RSD) for the duplicate samples was within 5%. Blank samples were also collected to check if there was any contamination during transport or any interference during sample analysis in the lab. No compounds were detected in the blank samples. Each day before sample analysis the analytical system was challenged first with a humidified zero air to ensure that the analytical system was clean, and then with a dynamically diluted 100 pptv standard mixture to check the performance of the system. If the

responses were not within 10% of the initial calibration curves, recalibration was conducted.

### 2.4. PMF Receptor Model

[14] PMF was used to better understand the halocarbons data obtained in 2001–2002 and in 2007 in the PRD region. Briefly, a mass balance equation can be written to account for all  $m$  chemical species in the  $n$  samples as mixing ratios from  $p$ -independent sources,

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij}, \quad (1)$$

where  $x_{ij}$  is the  $j$ th species mixing ratio measured in the  $i$ th sample,  $g_{ik}$  is the species contribution of the  $k$ th source to the  $i$ th sample,  $f_{kj}$  is the  $j$ th species fraction from the  $k$ th source,  $e_{ij}$  is residual associated with the  $j$ th species mixing ratio measured in the  $i$ th sample, and  $p$  is the total number of independent sources [Paatero, 1997]. PMF provides a matrix of the source profiles and a matrix of the time series of source mixing ratios without prior knowledge of halocarbon sources. In PMF, sources are constrained to have nonnegative species values, and no sample can have a negative source contribution. An “object function,”  $Q$ , that is to be minimized as a function of  $G$  and  $F$  is given by

$$Q(E) = \sum_{i=1}^m \sum_{j=1}^n \left[ \frac{e_{ij}}{s_{ij}} \right], \quad (2)$$

where  $s_{ij}$  is an estimate of the “uncertainty” in the  $j$ th variable measured in the  $i$ th sample. The factor analysis problem is then to minimize  $Q(E)$  with respect to  $G$  and  $F$  with the constraint that all of the halocarbons of  $G$  and  $F$  are to be nonnegative. PMF uses a unique algorithm in which both  $G$  and  $F$  matrices are varied simultaneously in each least squares step [see Paatero, 1997].

[15] To find the number of sources and their profiles, it is necessary to test different numbers of sources and find the optimal value with the most physically reasonable results. The results of the PMF analyses are not hierarchical, i.e., a higher-dimension solution does not necessarily contain all the factors of the lower dimensions. Thus, different numbers of factors were tested, and an optimum solution was determined based on both a good fit to the data and the most meaningful results. If the number of sources is estimated properly, the theoretical value of  $Q$  should be approximately equal to the number of degrees of freedom, or approximately equal to the total number of data points. However, if the number of sources is not well determined, the value of  $Q$  may deviate from the theoretical value.

## 3. Results and Discussion

### 3.1. General Features

[16] Table 1 summarizes the mean mixing ratios of halocarbons, together with the 95% confidence intervals, and median values at the two sites. The average subtropical Northern Hemisphere (NH) background values at the Mauna Loa station, Hawaii (19.54°N, 155.58°W), in the fall of 2007 obtained from the NOAA/ESRL halocarbon in situ program ([http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats\\_](http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats_)

**Table 1.** Mean Mixing Ratios of Halocarbons at WQS and TC, Together With Subtropical Northern Hemisphere Background Levels From NOAA

Common Name	Formula	Lifetime (years) <sup>a</sup>	ODP <sup>a</sup>	WQS		TC		Subtropical NH Background <sup>c</sup>
				Mean <sup>b</sup> (SD)	Median <sup>b</sup>	Mean <sup>b</sup> (SD)	Median <sup>b</sup>	
HCFC-22	CHClF <sub>2</sub>	12.0	0.055	438 (38)	388	574 (74)	427	188 (2.2)
CFC-11	CCl <sub>3</sub> F	45	1.0	277 (4)	277	273 (5)	273	247 (0.6)
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	100	1.0	614 (8)	609	587 (7)	589	539 (1.0)
CFC-113	CCl <sub>3</sub> CFClF <sub>2</sub>	85	0.8	95 (3)	91	92 (3)	90	79 (0.3)
Methyl chloride	CH <sub>3</sub> Cl	1.0		1085 (51)	1088	1091 (93)	1004	549 (2)
Methyl bromide	CH <sub>3</sub> Br	0.7	0.6	34 (3)	30	21 (2)	20	8 (0.03)
Carbon tetrachloride	CCl <sub>4</sub>	26	1.1	116 (3)	115	115 (5)	109	92 (0.6)
Methyl chloroform	CCl <sub>3</sub> CH <sub>3</sub>	5.0	0.1	53 (7)	47	32 (5)	24	12 (0.2)
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	0.01		511 (94)	391	70 (31)	27	1 <sup>d</sup>
Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	0.27		125 (23)	84	29 (9)	17	3.3 (0.4) <sup>e</sup>
Nitrogen oxides	NO <sub>x</sub>			34 (3)	8	44 (5)	32	
Ozone	O <sub>3</sub>			49 (7)	31	33 (3)	33	
Carbon monoxide	CO			1080 (64)	1005	453 (20)	428	
Sulfur dioxide	SO <sub>2</sub>			32 (3)	29	7 (0.5)	6	

<sup>a</sup>World Meteorological Organization [2003].<sup>b</sup>Measured in pptv. Numbers in parentheses are the standard deviations with a 95% confidence interval.<sup>c</sup>Subtropical NH background value from the NOAA/ESRL halocarbons in situ program, [http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats\\_conc.html](http://www.esrl.noaa.gov/gmd/hats/insitu/cats/cats_conc.html). The monthly mean values in November 2007 at Mauna Loa, Hawaii, were used. Measured in pptv.<sup>d</sup>Mean tropical surface (<1 km) mixing ratios summarized from the data of TRACE-P [Ko and Poulet, 2003].<sup>e</sup>Estimated subtropical background value from the UC-Irvine global monitoring program, <http://cdiac.ornl.gov/trends/otheratg/blake/data.html>. The monthly mean value in September 2007 at Baja, Mexico, was used.

conc.html) are also shown in Table 1. The NOAA/ESRL halocarbon in situ program does not measure short-lifetime substances such as TCE and PCE, and the surface mixing ratio of PCE was obtained in the autumn of 2007 from Baja, Mexico, an area with comparable latitudes (14.5°N–30°N) to the study region, from the UC-Irvine global monitoring network (<http://cdiac.ornl.gov/trends/otheratg/blake/data.html>) [Simpson *et al.*, 2004]. The TCE data were obtained from TRACE-P data (altitude <1 km) collected over western Pacific and the South China Sea (23.5°N–8°N) in April 2001 [Ko and Poulet, 2003]. Please note the TRACE-P data are for April, which matters for short-lived species such as TCE with strong seasonality. In April the background TCE mixing ratios are expected to have passed the seasonal winter maximum on their way to a summer minimum, and, compared to the large enhancements measured in the PRD, the effect of seasonality is expected to be minor compared to local source influences.

[17] The mean mixing ratios of CFC-12, CH<sub>3</sub>CCl<sub>3</sub>, CH<sub>3</sub>Br, TCE, and PCE at the WQS site were 1–7 times those at TC site (Table 1). However, the average HCFC-22 mixing ratio at WQS was only 0.76 times that at TC. HCFC-22 is the substitute of CFC-12, commonly used in commercial refrigeration units (e.g., in supermarkets) and air conditioning systems [McCulloch *et al.*, 2003; Stemmler *et al.*, 2004; Chan *et al.*, 2006]. The higher HCFC-22 level at TC was probably due to the earlier replacement of CFC-12 by HCFC-22 as Hong Kong is not an Article 5 party. In fact, the import of CFCs from overseas for local consumption in Hong Kong has been banned since 1996, while HCFCs are still imported for local consumption ([http://www.epd.gov.hk/epd/english/environmentinhk/air/ozone\\_layer\\_protection/wn6\\_info\\_phaseout\\_schedule.html](http://www.epd.gov.hk/epd/english/environmentinhk/air/ozone_layer_protection/wn6_info_phaseout_schedule.html)). In contrast, as a developing country, China still allows the production of CFCs, halons and other halocarbons under the terms of the Montreal Protocol and its amendments. Therefore, the higher CFC-12 average at WQS and higher HCFC-22 level at TC reflects the differences in use patterns and emis-

sion features of halocarbons between the two sites, and is an interesting reflection of the effect of the Montreal Protocol on Article 5 and non-Article 5 parties. The large discrepancy between median and mean values for HCFC-22, TCE and PCE suggested their nonnormal distributions.

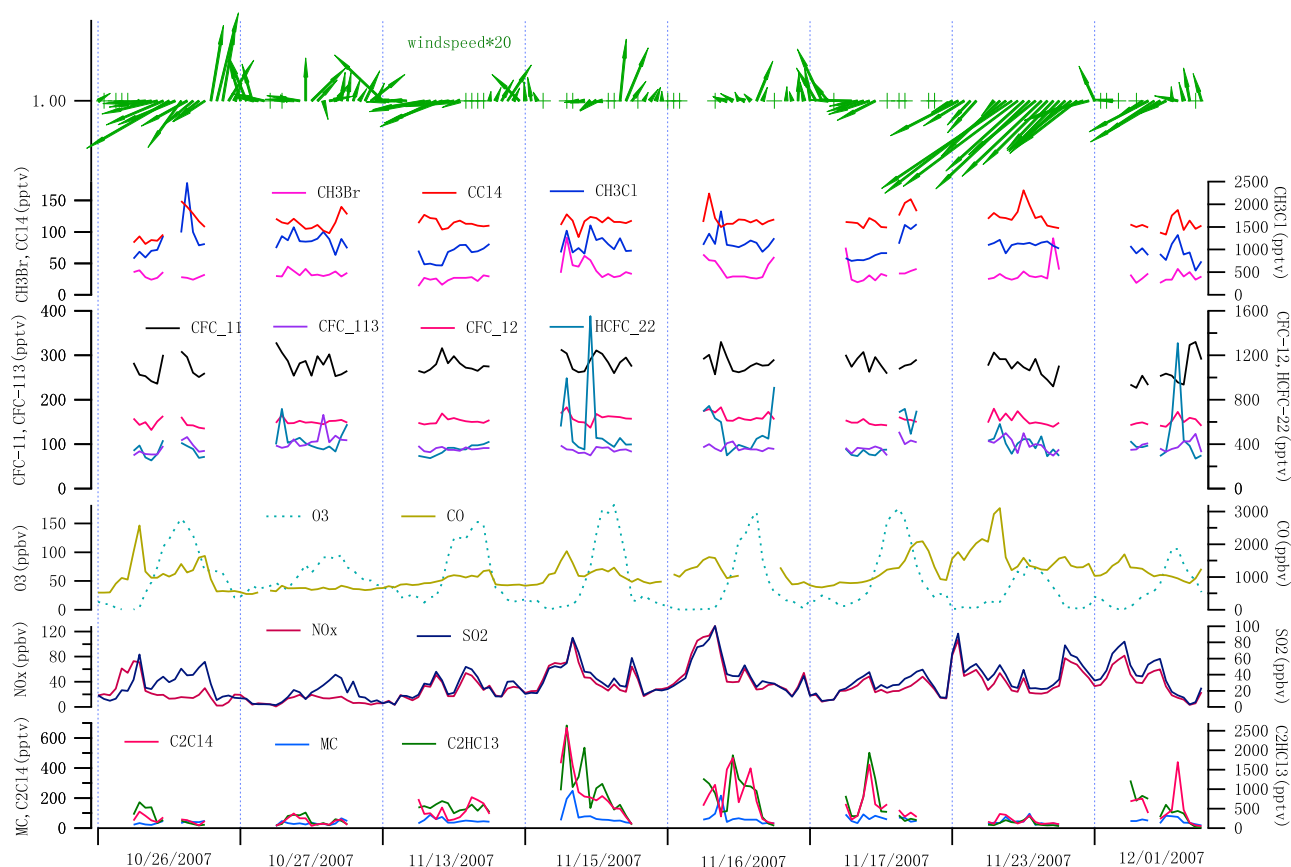
[18] Compared to the tropical NH surface background values, the mixing ratios of halocarbons at both sites were all much higher, suggesting significant contributions of continental emissions. Indeed, intensive halocarbon emissions from anthropogenic activities and typically less well mixed air masses lead to higher halocarbon values measured in the greater PRD region. Hence, we would expect a higher PRD background values than the global values. This was confirmed by Guo *et al.* [2009a], who found that the halocarbon levels over the South China Sea were higher than tropical NH background values.

### 3.2. Spatiotemporal Variations of Halocarbons in the Greater PRD Region

[19] Figures 2 and 3 show the daily patterns of halocarbons measured on sampling days between 26 October and 1 December 2007 at the WQS and TC sites, respectively. The time series of wind direction, wind speed, and other trace gases (e.g., O<sub>3</sub>, CO, SO<sub>2</sub> and NO<sub>x</sub>) are also shown in Figures 2 and 3. Figures 2 and 3 were drawn using hourly measurement data with the aid of Igor Plot software. The raw data for Figures 2 and 3 are provided as auxiliary material (Table S1).<sup>1</sup> It can be seen that there were no consistent diurnal variations for halocarbons and gaseous air pollutants at both sites. At WQS, the maximum O<sub>3</sub> mixing ratios on 27 October and 23 November were lower than 100 ppbv (i.e., low-O<sub>3</sub> days) whereas its levels on the other days were all above 100 ppbv (i.e., high-O<sub>3</sub> days) (Figure 2). Basically, regardless of high- or low-O<sub>3</sub> days, the average mixing ratios of long-lived CFCs, HCFC-22, CCl<sub>4</sub> and CH<sub>3</sub>Cl were con-

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2009JD013726.



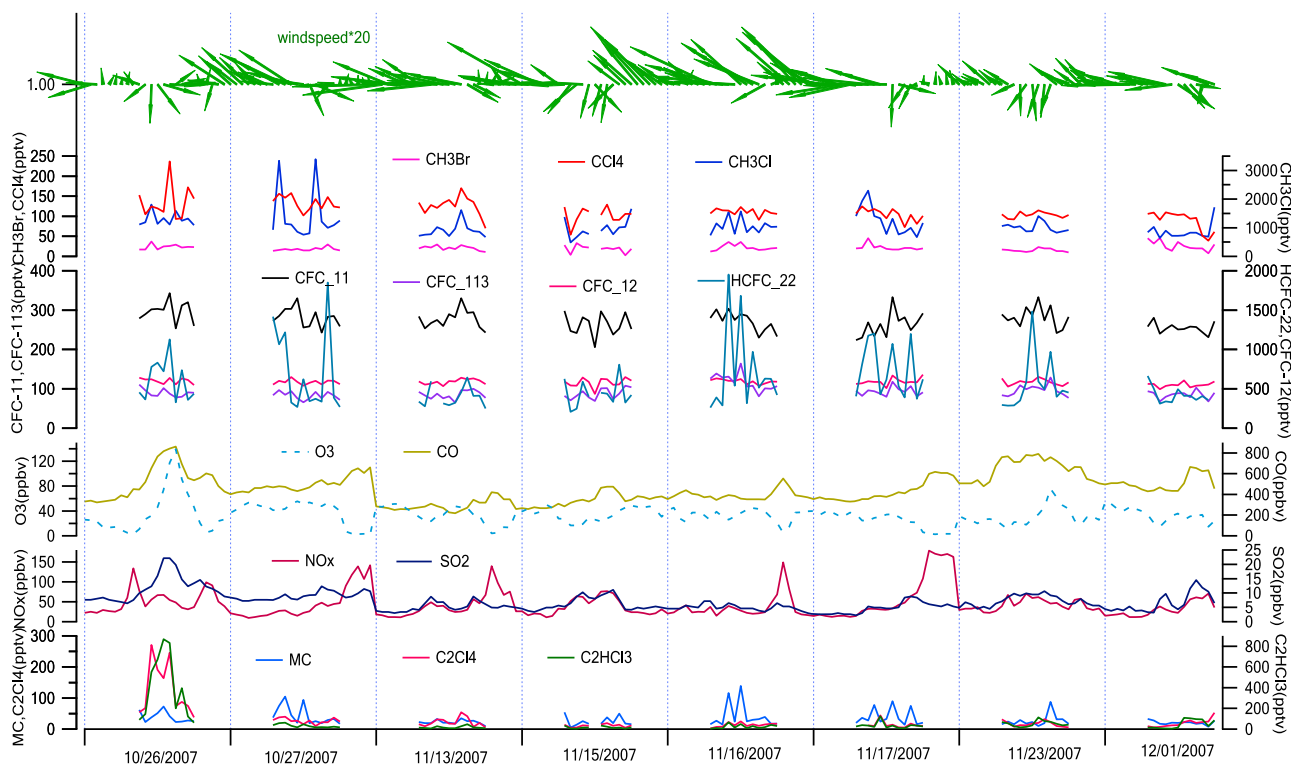


**Figure 2.** Temporal variations of halocarbons at WQS on 8 sampling days between 26 October and 1 December 2007. MC means methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ). The glitch with the wind barbs indicates the absence of wind data.

sistent due to the widespread use of these halocarbons in the region. However, the average mixing ratios of short-lived  $\text{CH}_3\text{CCl}_3$ ,  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{Cl}_4$  on low- $\text{O}_3$  days were lower than those on high- $\text{O}_3$  days ( $p < 0.05$ ). The low mixing ratios of the short-lived species on 27 October were mainly due to the dilution of clean marine air, whereas the low levels found on 23 November were predominantly caused by the elevated northeastern winds. In contrast, high levels of these short-lived species on high- $\text{O}_3$  days were mainly attributed to the local sources (such as on 26 October, 15–16 November), and regional transport (i.e., on 13 and 17 November).

[20] At the TC site, only on 26 October the maximum  $\text{O}_3$  mixing ratio was over 100 ppbv, and the  $\text{O}_3$  levels on other days were all below 100 ppbv (Figure 3). As was the case with those long-lived species at WQS, there was no significant difference between high- and low- $\text{O}_3$  days for CFCs, HCFC-22,  $\text{CCl}_4$  and  $\text{CH}_3\text{Cl}$ . On the other hand, the average mixing ratios of short-lived  $\text{CH}_3\text{CCl}_3$ ,  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{Cl}_4$  on high- $\text{O}_3$  days were higher than those on low- $\text{O}_3$  days (Figure 3). On 26 October, the diurnal trend of  $\text{CH}_3\text{CCl}_3$ ,  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{Cl}_4$  followed the pattern of primary pollutants such as  $\text{SO}_2$ , CO, and the secondary pollutant  $\text{O}_3$ , suggesting the influence of regional transport. The low mixing ratios of  $\text{CH}_3\text{CCl}_3$ ,  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{Cl}_4$  on low- $\text{O}_3$  days were likely due to the integrated impact of Asian monsoon circulation, strong vertical dispersion, high wind speeds and weak local emissions.

[21] Large day-to-day variations were observed for most halocarbons at both WQS and TC, in particular for HCFC-22 (340–555 pptv), TCE (130–1000 pptv), PCE (44–240 pptv),  $\text{CH}_3\text{Cl}$  (910–1210 pptv),  $\text{CH}_3\text{CCl}_3$  (35–80 pptv), and  $\text{CH}_3\text{Br}$  (30–45 pptv). In contrast, longer-lived species such as CFC-11, CFC-12, CFC-113 and  $\text{CCl}_4$  had relatively small day-to-day variations, with daily mean mixing ratios ranging from 260–285 pptv, 585–655 pptv, 85–110 pptv and 105–125 pptv, respectively. Further inspection found significant daily variations for most halocarbon species on 15–16 November at WQS, with relative standard deviations (RSDs) from 51%–76%, and on 16–17 November at TC, 1 day after that observed at WQS, with halocarbon RSDs between 34% and 88%. On 15–16 November at WQS, the wind was calm and the morning boundary layer height was low (less than 500 m; Figure 4), which was favorable to the accumulation of air pollutants. Indeed, morning maximum CO mixing ratios (1785 ppb and 1610 ppb, respectively) were found, as were  $\text{SO}_2$  (85 and 100 ppbv, respectively) and  $\text{NO}_x$  (110 and 130 ppbv, respectively).  $\text{O}_3$  levels reached 180 and 170 ppbv, respectively (Figure 2). On 16–17 November at TC, all the halocarbons, in particular HCFC-22, had larger daily variations than on other days except TCE and PCE, which had their largest daily variations on 26 October (Figure 3). For instance, the RSDs for HCFC-22 on 16 and 17 November were 89% and 74%, respectively. The prevailing wind direction was southeasterly from the South China Sea, which



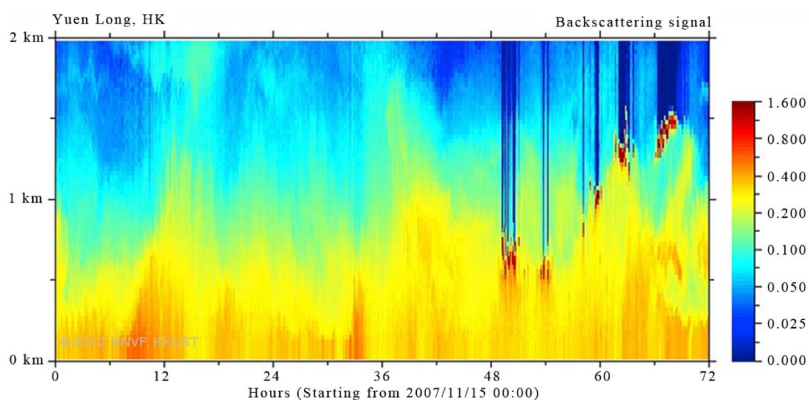
**Figure 3.** Temporal variations of halocarbons at TC on 8 sampling days between 26 October and 1 December 2007. MC means methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ).

caused the mixing ratios of other trace gases (i.e.,  $\text{CO}$ ,  $\text{SO}_2$  and  $\text{NO}_x$ ) to be much lower than those at WQS. For example, the maximum  $\text{CO}$  levels at TC were only 554 ppbv and 617 ppbv on 16 and 17 November, respectively. The different daily patterns at the two sites indicate the difference of emission patterns for different pollutants and the impact of meteorological conditions.

[22] Scatter plots (not shown here) of CFCs on individual sampling days showed that the correlation coefficients ( $R^2$ ) were 0.33–0.78, 0.34–0.70, and 0.26–0.55 for CFC-12 versus CFC-11, CFC-12 versus CFC-113, and CFC-11 versus CFC-113, respectively, at the TC site; and were 0.27–0.82, 0.27–0.56, and 0.16–0.52, respectively, at the WQS site. Days with good correlations among these CFCs suggest that they might originate from the same sources or from colocated

sources, or be used in the same pattern. Traditionally, these CFCs are used as refrigerants in cooling appliances and air conditioning and foam blowing agents [Aucott *et al.*, 1999; McCulloch *et al.*, 2001, 2003; Hurst *et al.*, 2006]. However, HCFC-22, a substitute of CFC-12 and mainly emitted from refrigeration units and air conditioning systems (section 3.1), did not show a similar daily emission pattern to the CFCs, most likely reflecting the fact that HCFC-22 and CFCs were not used by the same sources although they are all refrigerants. The similar daily patterns for CFC-11, CFC-12 and CFC-113 were also observed by Guo *et al.* [2009a].

[23] Relatively small daily variations of CFC-11 and CFC-12 were observed at both sites, suggesting the reduced frequency of their emissions, and to a lesser content, their long lifetimes (45 and 100 years, respectively). The sub-



**Figure 4.** Lidar-normalized relative backscattering signal on 15–16 November 2007.



tropical NH backgrounds of CFC-11 and CFC-12 were  $247 \pm 0.6$  and  $539 \pm 1.0$  pptv, respectively in fall 2007, based on measurements by the NOAA global monitoring network (Table 1). Therefore the CFC-11 and CFC-12 measurements from this study were enhanced by factors of 10%–11% and 8%–12%, respectively, over the background. The variability of CFC-11 (RSD = 14%) and CFC-12 (RSD = 8%) of the 100 samples at WQS was in line with the results observed in Guangzhou (RSD = 10% and 22%, respectively) and Xinken (RSD = 10% and 15%, respectively), but more variable than that in Taipei (RSD = 3% and 4%, respectively) [Chang *et al.*, 2008]. This is likely due to the different phase-out schedules between developed and developing countries. At TC, the variability of CFC-11 and CFC-12 was 12% and 8%, respectively, which was similar to that at WQS. Though Hong Kong is a non-Article 5 party, its geographical location is very close to the inland PRD. The similar variability of CFC-11 and CFC-12 at both sites suggests the influence of air masses from inland PRD on Hong Kong. Indeed, the particle release simulation results show that the air quality in Hong Kong was significantly affected by air pollution in eastern PRD [Guo *et al.*, 2009b]. In contrast, a large variability of HCFC-22 (RSD = 46% at WQS and 64% at TC) was found, indicating various strengths of its emission sources, and the influence of meteorological conditions on this halocarbon.

[24] CFC-113 mixing ratios at WQS and TC were enhanced compared to the tropical NH background (Table 1), and small variability (RSD = 13% and 14% at WQS and TC, respectively) were found at both sites. In light of the Montreal Protocol, CFC-113 has been replaced by its substitutes in developing countries including China [UNEP, 2003]. Due to its extremely long atmospheric lifetime (85 years), CFC-113 in the atmosphere declines at a slow rate.

[25] Relatively small temporal variations of  $\text{CCl}_4$  were detected at WQS and TC (RSD = 15% and 24%, respectively), perhaps due to its relatively long lifetime (26 years) and/or rare use of this compound in the PRD region nowadays. Though relatively small variability was found in this study, in 2000 large enhancements of  $\text{CCl}_4$  (RSD = 35% and mean mixing ratio of 138 pptv, versus 115 pptv in this study) were found in industrial areas of inland PRD. Similarly, in 2001 and 2004 large  $\text{CCl}_4$  variability was found in urban areas of Guangzhou (RSD = 45% and mean mixing ratio 156 pptv) [Chan and Chu, 2007; Chang *et al.*, 2008], implying that this halocarbon was still in use in inland PRD in recent years.

[26] The variability (i.e., RSD) of  $\text{CH}_3\text{CCl}_3$  (methyl chloroform, MC or MCF) at WQS and TC was 68% and 76%, respectively. These large variabilities of  $\text{CH}_3\text{CCl}_3$  were likely the result of different emission source strengths, various meteorological conditions and its relatively short lifetime (~5 years). The very short-lived halocarbons, i.e., TCE and PCE (lifetimes 0.01 and 0.27 years, respectively) showed large daily variations and similar temporal patterns ( $R^2 = 0.64$  and  $0.56$  at WQS and TC, respectively) (Figures 2 and 3). They are mainly used as cleaning solvents and are rapidly emitted into the atmosphere [Chan and Chu, 2007]. In inland PRD, TCE is used as a cleaning solvent in the electronics industry [He *et al.*, 2002; Chan and Chu, 2007], whereas TCE and PCE are often used as dry cleaning agents in Hong Kong.

[27] As the most abundant halocarbon in the atmosphere,  $\text{CH}_3\text{Cl}$  has various anthropogenic sources, i.e., biomass burning and biofuel use including coal burning, and natural sources such as tropical plants and the oceans [Blake *et al.*, 1996; McCulloch *et al.*, 1999; Warneck, 2000; Yokouchi *et al.*, 2000, 2002a]. Hence, the  $\text{CH}_3\text{Cl}$  distribution was more complicated than other halocarbons. The mixing ratio of  $\text{CH}_3\text{Cl}$  varied from day-to-day and hour-to-hour at both sites, implying the complexity of  $\text{CH}_3\text{Cl}$  sources in this region. Chan and Chu [2007] indicated that emissions from paper factories enhanced  $\text{CH}_3\text{Cl}$  levels in the PRD region. The enhancements could also be related to exhaust from coal-fueled boilers, which provide heat and steam for cooking pulp and drying paper [U.S. Environmental Protection Agency, 2002]. In addition, elevated  $\text{CH}_3\text{Cl}$  levels were probably caused by the power plant in Humen town of Dongguan, approximately 10 km to the southeast of WQS, which uses coal as fuel for power generation. In our study, poor correlation was found between  $\text{CH}_3\text{Cl}$  and HCFC-22, an urban tracer ( $R^2 = 0.2$  at WQS and  $0.1$  at TC), suggesting different anthropogenic sources. Guo *et al.* [2009a] estimated that about 40% of the  $\text{CH}_3\text{Cl}$  in the greater PRD originated from industrial usage and 48% from biomass/biofuel burning.

[28] Infrequent and rare use of  $\text{CH}_3\text{Br}$  resulted in minor temporal variations on the sampling days at both sites though its lifetime is relatively short (0.7 years). Some spikes at WQS were likely due to soil fumigation, as considerable agricultural activities are widely distributed around the PRD [Chan and Chu, 2007].

### 3.3. Change of Emission Source Profiles Between 2001 and 2007

[29] Prior to this work, a 16 month field measurement was carried out in 2001–2002 in the study region [Guo *et al.*, 2009a]. This provides us an opportunity to evaluate the change of emission source profiles in the past 6 years. Since the sampling period in this study was from October to December, we chose the measurement data collected in the same periods, i.e., October–December, from the 2001–2002 study for comparison. In total, 71 samples were taken in that period in 2001 and 2002. To obtain robust modeling and statistical results, we performed PMF modeling on the 71 samples in 2001–2002, and the 194 samples in 2007. Eight main halocarbons were selected for the analysis since they are the species available in both studies. After running the PMF model, five sources were identified in the PRD region in the 2001–2002 study and this study (Table 2 and Figure 5).

[30] Detailed source identification can be found in Guo *et al.* [2009a]. In brief, the emission sources of halocarbons in 2007 remained the same as those in 2001–2002 in the study region. The first source in both studies was an industrial source related to refrigerant production, which is characterized by a high mass percentage of CFC-11, CFC-12 and CFC-113, as well as  $\text{CCl}_4$  and  $\text{CH}_3\text{Cl}$  [Altshuller, 1976; Aucott *et al.*, 1999; McCulloch *et al.*, 2001, 2003; Sturrock *et al.*, 2002; HKEPD, 2005a]. The high correlation between  $\text{CCl}_4$  and CFCs suggests that this source was more related to the production than the consumption of refrigerants.

[31] The second source was distinguished by a high mass percentage of  $\text{C}_2\text{HCl}_3$  (63%–84%) in both studies. In the

**Table 2.** Source Profiles of Halocarbons in the PRD Region in 2001–2002 and in 2007<sup>a</sup>

	CFC12	CFC11	CFC113	HCFC22	CCl4	C <sub>2</sub> HCl <sub>3</sub>	C <sub>2</sub> Cl <sub>4</sub>	CH <sub>3</sub> Cl
<i>Refrigeration Industry (source 1)</i>								
2001–2002	276 ± 24	140 ± 12	37 ± 3	0 ± 14	59 ± 5	3 ± 5	3 ± 2	277 ± 38
2007	488 ± 33	221 ± 19	73 ± 4	213 ± 30	82 ± 5	35 ± 6	0 ± 1	341 ± 47
<i>Metal Degreaser and Dry Cleaning (source 2)</i>								
2001–2002	86 ± 18	45 ± 9	15 ± 2	1 ± 12	21 ± 4	287 ± 14	1 ± 10	132 ± 29
2007	8 ± 12	3 ± 5	0 ± 2	11 ± 5	1 ± 2	252 ± 7	26 ± 8	33 ± 13
<i>Biomass and Biofuel Burning (source 3)</i>								
2001–2002	32 ± 24	20 ± 12	10 ± 3	20 ± 17	10 ± 5	0 ± 9	19 ± 5	333 ± 48
2007	3 ± 20	6 ± 10	5 ± 3	25 ± 10	10 ± 4	4 ± 2	0 ± 1	508 ± 34
<i>Solvent Use in Electronic Industry (source 4)</i>								
2001–2002	62 ± 18	25 ± 9	12 ± 2	72 ± 15	10 ± 4	164 ± 23	121 ± 5	1 ± 29
2007	97 ± 27	42 ± 20	14 ± 4	49 ± 9	18 ± 4	4 ± 10	53 ± 10	125 ± 54
<i>Replacement CFC (source 5)</i>								
2001–2002	156 ± 18	67 ± 9	25 ± 3	196 ± 12	23 ± 4	1 ± 5	23 ± 7	219 ± 38
2007	1 ± 15	2 ± 6	2 ± 2	206 ± 29	3 ± 2	4 ± 2	0 ± 1	80 ± 22

<sup>a</sup>Mean ±95% confidence interval. For 2001–2002,  $n = 71$ ; for 2007,  $n = 194$ . Measured in pptv.

PRD region, C<sub>2</sub>HCl<sub>3</sub> is substantially used as a degreasing solvent in electronic and textile industries and as a dry cleaning agents in laundries [He *et al.*, 2002; HKEPD, 2005b; Chan and Chu, 2007].

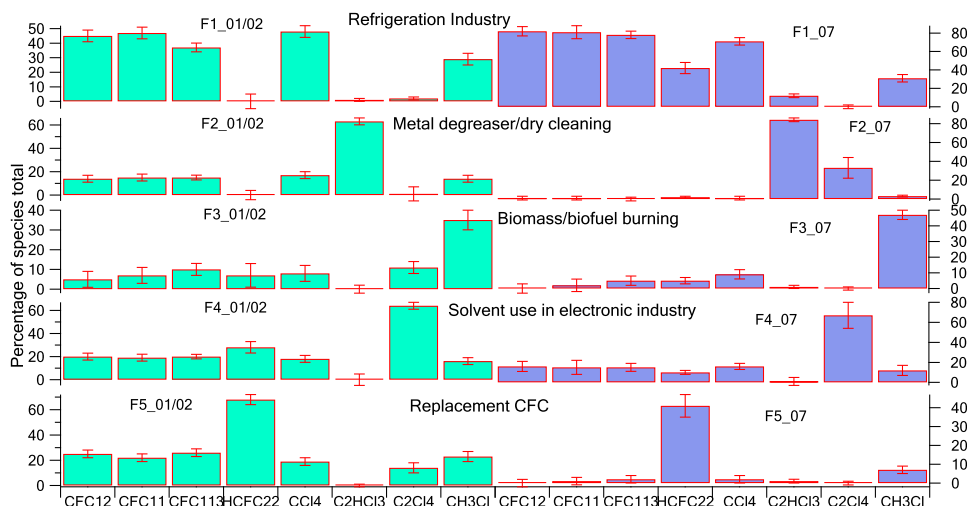
[32] The third source was characterized by a high mass percentage of CH<sub>3</sub>Cl (35%–47%) and CO (not shown here) in both studies, suggesting the strong influence of biomass/biofuel and/or coal burning of this source in the PRD region [e.g., Blake *et al.*, 1996; McCulloch *et al.*, 1999].

[33] A high percentage of C<sub>2</sub>Cl<sub>4</sub> (67%–72%) was observed in the fourth source in both studies. C<sub>2</sub>Cl<sub>4</sub> is used primarily as a surface degreasing agents and dry cleaning fluid [Simmonds *et al.*, 2006]. In inner PRD cities, in particular Dongguan, a city with many light industries (e.g., electronic computers, peripherals, and soldering machinery (Hong Kong Trade Development Council PRD economic profile available at <http://www.tdctrade.com/mktprof/china/prd.htm>), C<sub>2</sub>Cl<sub>4</sub> is widely used as an industrial cleaning solvent. This source

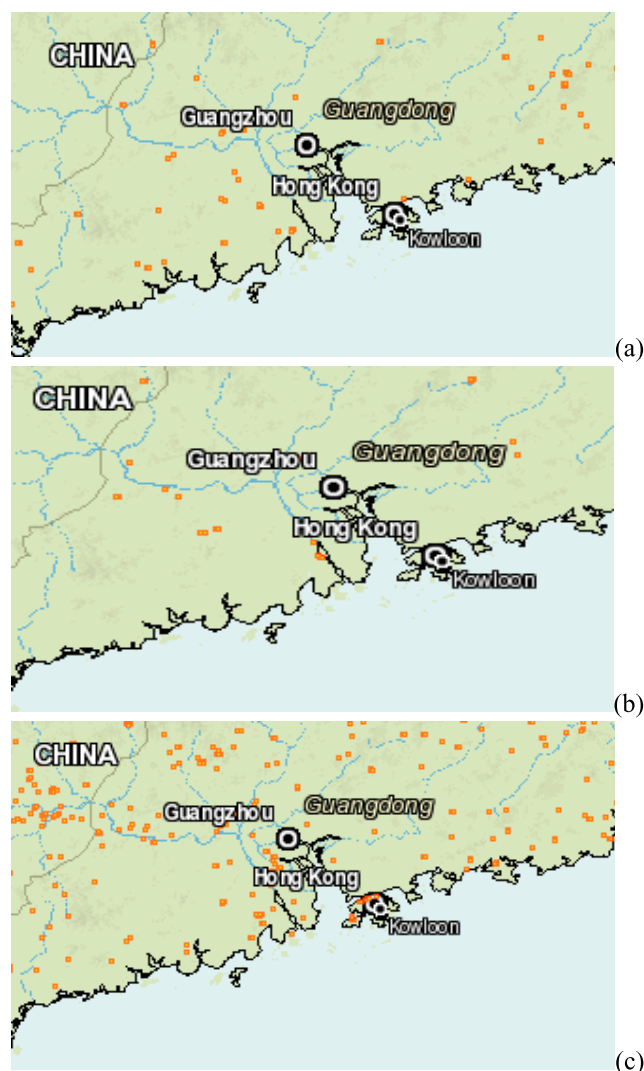
was most likely related to solvent use in the electronic industry.

[34] The last source showed a high mass percentage of HCFC-22 (41%–68%) in both studies. HCFC-22, substitute of CFC-12, is mainly emitted from refrigeration units and air conditioning systems [Aucott *et al.*, 1999; McCulloch *et al.*, 2003]. We classified this source as the replacement of CFCs.

[35] Although the emission sources of halocarbons in the PRD region remained the same from 2001–2002 to 2007, some remarkable changes in the source profiles were observed. The emissions of CFCs (i.e., CFC-11, -12, and -113) and CCl<sub>4</sub> from the refrigeration industry in 2007 were 1.4–2.0 times those in 2001–2002, in spite of the fact that the mixing ratios of these halocarbons did not change too much in the past 6 years. This may indicate that less of these halocarbons were used in other emission sources in 2007 than in 2001–2002. In addition, the substitute of CFC-12, i.e.,



**Figure 5.** Source profiles resolved from PMF in the PRD region in October–December of 2001–2002 (left,  $n = 71$ ) and of 2007 (right,  $n = 194$ ).



**Figure 6.** MODIS fire maps in the autumn season in the PRD region: (a) 2001; (b) 2002; (c) 2007. The red spots in the maps represent the fire events.

HCFC-22, accounted for 42% of the species total in the refrigeration industry in 2007, compared to a nil percentage in the same source in 2001–2002. The results reflect the transition of refrigerants from CFCs to HCFCs in the refrigeration industry, and the widely mixed use of CFCs and HCFCs in the production of refrigeration in the PRD region.

[36] Compared to the mixing ratios of cleaning agents, i.e.,  $C_2HCl_3$  and  $C_2Cl_4$ , their levels in 2007 were only 0.7 and 0.5 times those in 2001–2002, respectively. In particular, their use in electronic industry as solvents has been significantly reduced in the past 6 years ( $p < 0.01$ ), while the source of metal degreaser/dry cleaning has slightly cut the use of these two halocarbons (Table 2).

[37] Though the emission of HCFC-22 from the fifth source remained unchanged in the past 6 years ( $196 \pm 12$  pptv in 2001–2002,  $206 \pm 29$  pptv in 2007), its mixing ratio in the atmosphere actually increased from 290 pptv in 2001–2002 to 503 pptv in 2007, suggesting that on one hand emissions from the consumption of refrigeration units and air conditioning systems were constant, and on the other

hand, there were other sources that caused the increase in HCFC-22 mixing ratio. As described above, significant HCFC-22 emission ( $213 \pm 30$  pptv) was from the first source in 2007, implying the increased use of HCFC-22 in the production of refrigeration in inland PRD region in recent years.

[38] As discussed in our previous work,  $CH_3Cl$  was mainly emitted from the production of refrigerants and biomass/biofuel burning in the study region [Guo *et al.*, 2009a]. During the past 6 years, the contribution from the refrigeration industry to ambient  $CH_3Cl$  did not have significant changes. However, the contribution from biomass/biofuel and coal burning increased from  $333 \pm 48$  pptv in 2001–2002 to  $508 \pm 34$  pptv in 2007, suggesting the increased activities of biomass/biofuel burning. Indeed, the MODIS fire maps show many more fire spots in autumn 2007 than in autumn 2001 and 2002 (<http://firefly.geog.umd.edu/firemap/>) (Figure 6).

### 3.4. Annual Trends of Halocarbons in the Greater PRD Region

[39] Understanding the annual variations of major halocarbons is critical to the long-term implementation and refinement of control measures. Though Hong Kong is part of the greater PRD, it is a non-Article 5 party while the inland PRD region is an Article 5 party (section 1). This provides us an excellent chance to contrast the differences between the two parties. Fortunately, since 1998 measurements of halocarbons have been carried out by different research teams in the PRD region, and most of these air samples have been analyzed on the same analytical system at UCI. Therefore, there is an internal consistency to many of the measurements that allow for direct intercomparison. Tables 3 and 4 provide the details of these halocarbon data collected in different years by different groups. For the samples collected in Hong Kong (Table 3), most of them were mainly taken in western Hong Kong (i.e., Tai O, also on Lantau Island, and Tung Chung) and analyzed at UCI. It should be noted that the methodology for instrumental analysis of halocarbons used in this study (by GIG) was established with the help of UCI. The interlab comparison between these two labs agreed well ( $RSD \leq 5\%$  for the target halocarbons except  $CCl_4$ , its  $RSD = 12\%$ ). On the other hand, the inland PRD samples were mainly taken in the Guangzhou urban area (in 2000 and 2005) and in the Guangzhou rural area (i.e., at WQS in 2004 and 2007) (Table 4). Since there were no measurements conducted in 2001–2003 in inland PRD, we used the data collected at Tai O of western Hong Kong, which is downwind of inland PRD in autumn. Back trajectory analysis on the air samples collected at Tai O in 2001–2002 was undertaken to distinguish the air masses from the inland PRD. Although there were no overlapping field sampling campaigns in inland PRD in 2001–2002 when the halocarbon data were collected at Tai O, an intensive field measurement was conducted in Guangzhou of inland PRD in spring 2001 [Chan *et al.*, 2006]. The mean values of main halocarbons such as CFCs, HCFC22,  $CH_3Cl$ ,  $CCl_4$ ,  $C_2Cl_4$  and  $CH_3CCl_3$  in the Guangzhou study were comparable to those at Tai O, which using back trajectory analysis were classified as air masses from inland PRD, suggesting that these Tai O data were representative of inland PRD air. Bearing the above facts in

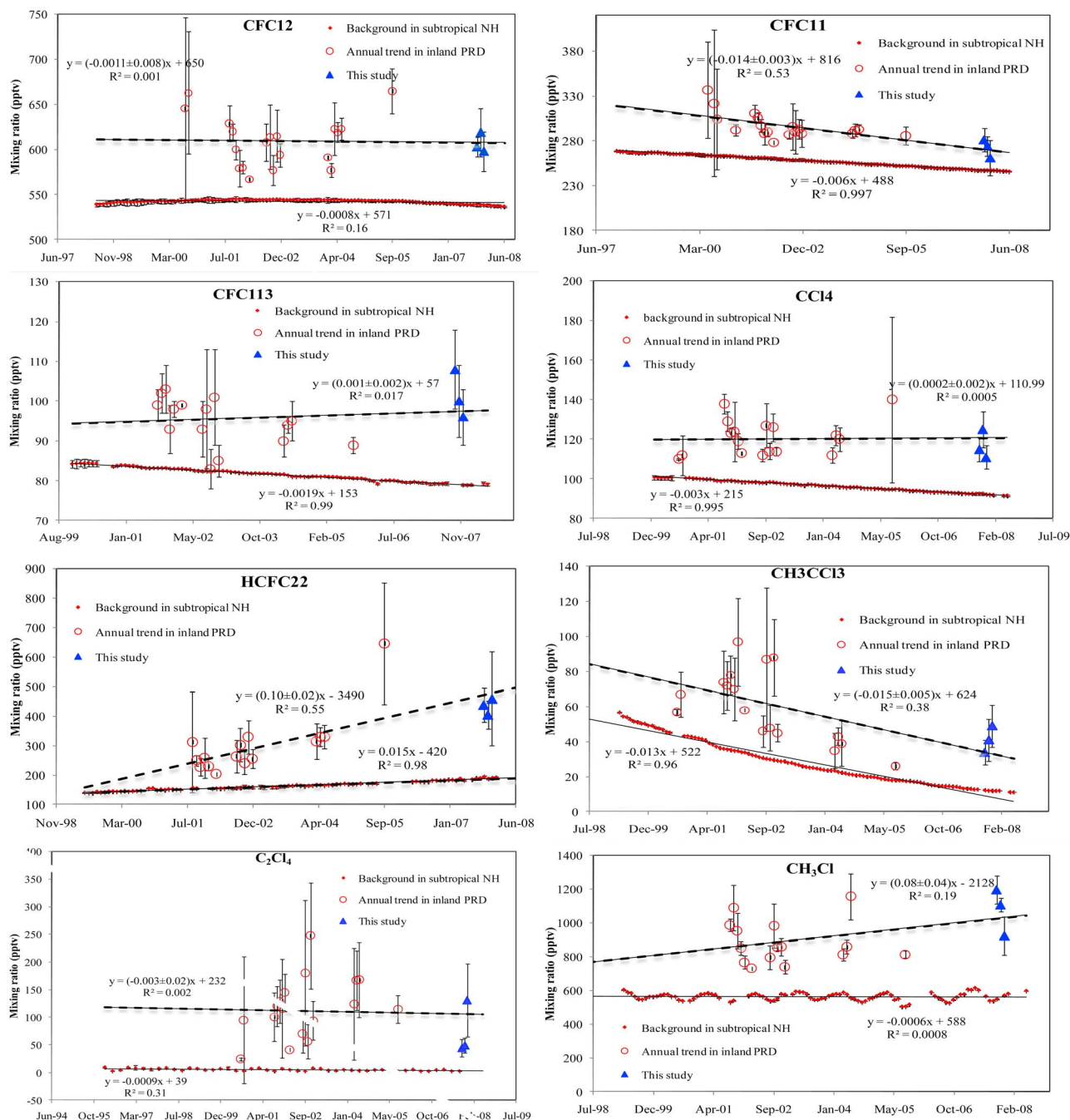


Figure 7. Annual trends of halocarbons in inland PRD.

mind, we present the monthly mean mixing ratios with error bars (95% confidence interval) of eight key halocarbon species in inland PRD from 2000 to 2007 and in Hong Kong from 1998 to 2008, respectively (Figures 7 and 8). It is noteworthy that in this study only data collected on non- $O_3$  episode days were used in Figures 7 and 8 to reflect the annual trend. For instance, the maximum  $O_3$  levels were higher than 100 ppbv at both sites on 26 October but were much lower on 27 October (see Figures 2 and 3). Hence, the data collected on 27 October were used for the monthly average calculation. It should also be noted that the halo-

carbon levels in the atmosphere are related to many factors such as the strengths and variations of local sources, regional transport, photochemical destruction, sampling seasons, sampling locations, and meteorological conditions. Some or all of the above factors need to be taken into account during annual trend analyses. For comparison, the monthly variations of target halocarbons at NOAA and UCI background sites with similar latitude to our sampling sites in 1998–2008 are also presented in Figures 7 and 8 (<http://www.esrl.noaa.gov/gmd/> and <http://cdiac.ornl.gov/trends/otheratg/blake/data.html>).



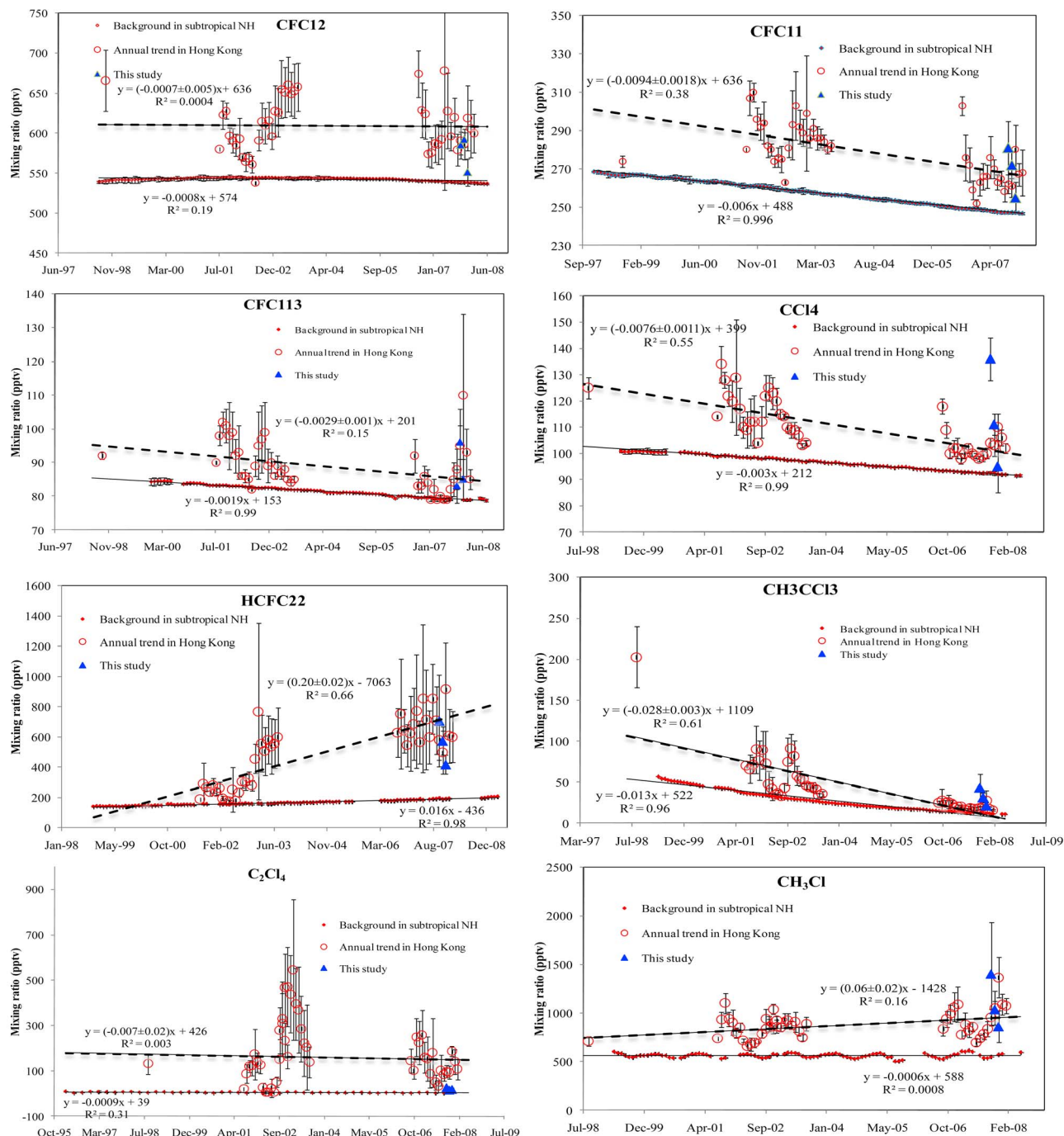


Figure 8. Annual trends of halocarbons in Hong Kong.

[40] It can be seen that CFC-11 and CFC-12 in inland PRD showed a general decreasing trend, and CFC-113 and CCl<sub>4</sub> basically remained consistent, reflecting the effective control of halocarbons in inland PRD in recent years (Figure 7). Compared to the annual trend of background values in subtropical North Hemisphere, the decreasing rates of CFC-11 and CFC-12 were much higher in the study region, particularly for CFC-11 (Table 5). In contrast, the mixing ratios of CFC-113 and CCl<sub>4</sub> in the study region slightly increased with very small rates while the subtropical background levels decreased. Although the Montreal Pro-

tol requires the Chinese government to phase out CFCs and CCl<sub>4</sub> by 2010, the Chinese government actually started to reduce its total consumption of CFCs in 2000 [State Environmental Protection Administration, 2000]. For instance, the total consumption of CFC-11 in China was targeted to be 22,850; 10,345; and 4,590 ODP metric tons in years 1999, 2005, and 2007, respectively. As a CFC replacement, HCFC-22 appeared to have an increasing trend in the past, consistent with the fact that the targeted production in China has been significantly increased from 15,000 metric tons in 1999 to 33,000 metric ton in 2007.



**Table 3.** Details of the Halocarbon Samples Collected in Different Years in Hong Kong

Year	Sampling Site <sup>a</sup>	Sample Size	Sampling Period	Sample Analysis	Remark
1998	Hong Kong/11 sites	72	Sep.	Canister, UCI	Blake's group, unpublished data
2001	Tai O, Hong Kong	59	Aug.–Dec.	Canister, UCI	<i>Guo et al.</i> [2009a]
2002	Tai O/ 4 HKEPD sites	129/89	Jan.–Dec. and Sep.–Dec.	Canister, UCI	<i>Guo et al.</i> [2009a]/Blake's group
2003	4 HKEPD sites	60	Jan.–Aug.	Canister, UCI	Blake's group
2006	4 HKEPD sites	64	Sep.–Dec.	Canister, UCI	Blake's group
2007	Tung Chung/4 HKEPD sites	98/141	Oct.–Dec. and Jan.–Dec.	Canister, GIG <sup>b</sup> /Canister, UCI	this study/Blake's group
2008	4 HKEPD sites	32	Jan.–Feb.	Canister, UCI	Blake's group

<sup>a</sup>The four HKEPD sites include Tung Chung, Yuen Long, Tap Mun, and central and western sites.

<sup>b</sup>Guangzhou Institute of Geochemistry.

Compared to the trend of the subtropical background (slope = 0.015 pptv/month  $\times$  12 = 0.18 pptv/yr), the increasing rate of HCFC-22 in inland PRD was much higher (slope = 1.2 pptv/yr,  $p < 0.01$ ). On the other hand, halocarbon species mainly emitted from industrial solvent usage such as  $\text{CH}_3\text{CCl}_3$  and  $\text{C}_2\text{Cl}_4$  in inland PRD showed much higher mixing ratios than subtropical background values ( $p < 0.01$ ), reflecting the fact that large amounts of these halocarbons were still in use in this rapidly developing region. The large monthly and seasonal variations of  $\text{CH}_3\text{CCl}_3$  and  $\text{C}_2\text{Cl}_4$  suggested the influence of emission source strength, meteorological conditions and photochemical reactions (i.e., larger variability due to shorter atmospheric lifetimes). Moreover, the decreasing rate of  $\text{CH}_3\text{CCl}_3$  in the inland PRD (slope =  $-0.18$  pptv/yr) was consistent with that in subtropical background North Hemisphere (slope =  $-0.16$  pptv/yr), whereas  $\text{C}_2\text{Cl}_4$  decreased with time at a rate of 0.036 pptv/yr, which is 3 times that of North Hemisphere subtropical background  $\text{C}_2\text{Cl}_4$  (slope =  $-0.011$  pptv/yr). Having complicated anthropogenic and natural sources,  $\text{CH}_3\text{Cl}$  presented an increasing trend from 2000 to 2007 (0.96 pptv/yr in inland PRD), though its background level in the subtropical North Hemisphere was much lower (about 588 pptv) and was still decreasing with a rate of 0.007 pptv/yr. The result suggests that more  $\text{CH}_3\text{Cl}$  might have been used in industries and/or emitted from biomass burning in inland PRD in recent years. *Guo et al.* [2009a] reported that about 40% of  $\text{CH}_3\text{Cl}$  in the study region originated from industrial use and 48% was due to the influence of biomass/biofuel and/or coal burning. The increase of  $\text{CH}_3\text{Cl}$  in inland PRD is consistent with the increase in coal consumption in China since 2000 [*National Bureau of Statistics of China*, 2008], while the inland PRD is the most rapidly developing region in China.

[41] In Hong Kong, CFC-12, CFC-11, and CFC-113 showed a decreasing trend with time, consistent with the temporal trend of subtropical background air in the Northern Hemisphere, and in line with the Montreal Protocol for developed countries/regions which phased out CFCs in 1997 (Figure 8 and Table 5). However, the mixing ratios of the

three CFC species in Hong Kong were still higher than the subtropical background levels in North Hemisphere ( $p < 0.05$ ), suggesting the potential impact from the developing inland PRD region and/or the release from existing CFC containing refrigerators and air conditioning systems in Hong Kong. Indeed, many CFC containing air conditioners are still in use in Hong Kong residences ([http://www.epd.gov.hk/epd/english/resources\\_pub/publications/files/pn94\\_4.pdf](http://www.epd.gov.hk/epd/english/resources_pub/publications/files/pn94_4.pdf)), consistent with the fact that elevated CFC-11 and CFC-12 levels were often observed in summer and autumn. In addition, compared to the subtropical background values, the three CFC species showed apparent seasonal variations in Hong Kong. Similarly, the  $\text{CCl}_4$  presented a decreasing trend in recent years in Hong Kong. Its decreasing rate (0.09 pptv/yr) is more than twice that of the subtropical background in North Hemisphere (0.04 pptv/yr). The  $\text{CCl}_4$  mixing ratios observed in Hong Kong were consistently higher than the subtropical background levels in recent years. Furthermore, the seasonal trend of  $\text{CCl}_4$  in Hong Kong was clear: high in autumn and winter and low in summer, in line with the influence of Asian Monsoon circulation. Contrary to the CFCs and  $\text{CCl}_4$ , the HCFC-22 mixing ratio increased at a rate of 2.4 pptv/yr, more than 12 times that of the subtropical background levels in North Hemisphere (0.18 pptv/yr), indicating significantly increased application of HCFCs as refrigerants in Hong Kong. Indeed, the monthly average of HCFC-22 in Hong Kong was about 100 pptv above the background level ( $\sim 150$  pptv) in the subtropical North Hemisphere in 2001–2002, but became much higher (over 400 pptv) than the subtropical background in 2006/07 ( $p < 0.01$ ). Bearing its large variation in mind,  $\text{CH}_3\text{CCl}_3$  showed a remarkable decreasing trend from September 1998 ( $203 \pm 37$  pptv) to February 2008 ( $16 \pm 1$  pptv) with a decreasing rate of 0.34 pptv/yr. Its monthly average values have been close to the North Hemisphere subtropical backgrounds since 2006, suggesting a gradual phase out of this solvent species in Hong Kong. In addition, the decreasing rate of  $\text{CH}_3\text{CCl}_3$  in Hong Kong was twice that of the subtropical background (0.16 pptv/yr). Similar to the inland PRD, large seasonal variations of  $\text{C}_2\text{Cl}_4$  were found in Hong Kong. The  $\text{C}_2\text{Cl}_4$

**Table 4.** Details of the Halocarbon Samples Collected in Different Years in Inland PRD

Year	Sampling sites	Sample size	Sampling period	Sample analysis	Remark
2000	Guangzhou urban area/19 sites	19	Aug.–Sep.	Canister, UCI	Blake's group, unpublished data
2001	Tai O	38	Sep.–Dec.	Canister, UCI	<i>Guo et al.</i> [2009a]
2002	Tai O	56	Jan.–Dec.	Canister, UCI	<i>Guo et al.</i> [2009a]
2004	WQS	88	Apr.–Jun.	Canister, UCI	T. Wang, personal communication (2009)
2005	Guangzhou urban area/7 sites	42	Sep.	Canister, UCI	Blake's group, personal communication
2007	WQS	100	Oct.–Dec.	Canister, GIG	this study

**Table 5.** Derived Slopes of the Target Halocarbons in Figures 7 and 8<sup>a</sup>

Halocarbon	Inland PRD		Hong Kong		NH background	
	Slope	Trend	Slope	Trend	Slope	Trend
CFC12	$-0.0011 \pm 0.008$	decrease	$-0.0007 \pm 0.005$	decrease	$-0.0008 \pm 0.0002$	decrease
CFC11	$-0.014 \pm 0.003$	decrease	$-0.0094 \pm 0.0018$	decrease	$-0.006 \pm 0$	decrease
CFC113	$0.001 \pm 0.002$	increase	$-0.003 \pm 0.001$	decrease	$-0.0019 \pm 0$	decrease
CCl <sub>4</sub>	$0.0002 \pm 0.002$	increase	$-0.0076 \pm 0.0011$	decrease	$-0.003 \pm 0$	decrease
HCFC22	$0.10 \pm 0.02$	increase	$0.20 \pm 0.02$	increase	$0.015 \pm 0.0003$	increase
CH <sub>3</sub> CCl <sub>3</sub>	$-0.015 \pm 0.005$	decrease	$-0.028 \pm 0.003$	decrease	$-0.013 \pm 0.0003$	decrease
C <sub>2</sub> Cl <sub>4</sub>	$-0.003 \pm 0.02$	decrease	$-0.007 \pm 0.02$	decrease	$-0.0009 \pm 0.0002$	decrease
CH <sub>3</sub> Cl	$0.08 \pm 0.04$	increase	$0.06 \pm 0.02$	increase	$-0.0006 \pm 0.002$	decrease

<sup>a</sup>Measured in pptv/month. Slope has mean  $\pm 95\%$  confidence interval.

mixing ratio decreased at a small rate of 0.08 pptv/yr in Hong Kong, eight times that of the subtropical background value. For the most abundant halocarbon, CH<sub>3</sub>Cl, its level increased with time at a rate of 0.72 pptv/yr, in line with that in inland PRD. Contrary to the Hong Kong area, the subtropical background CH<sub>3</sub>Cl level showed a decreasing trend in the past 10 years.

[42] Overall, the annual trends of halocarbons with long lifetime such as CFCs and HCFC-22 in Hong Kong were similar to that in inland PRD, suggesting significant interaction of air masses between inland PRD and Hong Kong. Indeed, during autumn/winter monsoon circulations, the air masses in Hong Kong were often affected by inland PRD. In contrast, Hong Kong air masses influence the inland PRD in summer. This was evidenced by Guo *et al.* [2009a].

#### 4. Conclusions

[43] A comprehensive dataset of halocarbons was collected at Wan Qing Sha (WQS) in inland PRD and Tung Chung (TC) in Hong Kong in October–December 2007. The mean values of CFC-12, CH<sub>3</sub>CCl<sub>3</sub>, CH<sub>3</sub>Br, TCE and PCE at WQS were 1–7 times those at TC, while HCFC-22 level at TC was 1.5 times that at WQS. The spatiotemporal variations indicated that CFC-11, CFC-12 and CFC-113 had similar temporal patterns with small variability, suggesting similar sources or use patterns or sink behavior of these species. On the other hand, TCE and PCE showed a large variability, implying the influence of emission sources, meteorological parameters and photochemical reactivity. In order to better understand the change of emission source profiles in the past years, receptor modeling analysis was carried out and the results indicated that the use of HCFC-22 in the production of refrigeration has significantly increased from 2001 to 2007 and its emission from the consumption of refrigeration units and air conditioners remained constant, whereas the application of C<sub>2</sub>HCl<sub>3</sub> and C<sub>2</sub>Cl<sub>4</sub> into the electronic industry was reduced remarkably. Though the levels of CFCs and CCl<sub>4</sub> in the atmosphere were slightly reduced, they showed increased use in the refrigeration industry but reduced emissions in other sources in the past 6 years. In addition, the contribution of biomass/biofuel burning to ambient CH<sub>3</sub>Cl has been significantly increased since 2001. By analyzing the halocarbon data collected in the past decade, we obtained the annual tendency of major halocarbons in the region for the first time. The annual trends showed that the mixing ratios of CFC-12 and -11 have been steadily declining since 2001, while their substitute HCFC-22 has had

a remarkable increase during these years, especially in Hong Kong.

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